HOWARD

The corrosion of iron and its alloys

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THE CORROSION OF IRON AND ITS ALLOYS

BY

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

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CORROSION OF IRON AND ITS ALLOYS.

In nature everything is subject to deterioration, varying from those substances decomposed by light to those only decomposed by the strongest agents. The deterioration of metals as effected by alloying is the subject of this paper and perhaps no subject is of more vital importance to the builder and interest to the chemist than this one of corrosion. It is a difficult matter to make a study of this kind of any practical value because of the difference in condition imposed upon the sample in the laboratory and when in actual use. An example of this disagreement between laboratory results and practical experience is very well demonstrated in the report "The Use of Concrete in Sea Water". From the laboratory experiment it was found that concrete could not be used in sea water; but as a matter of fact it is used, and with good results.

To explain this phenomonen different theories have been advanced. It is a well known fact that under certain conditions the impurities in a metal, causing segregation, are a cause of corrosion. However, favorable conditions must prevail before the process begins. A primary prerequisite to corrosion is moisture; however, it is unable to effect the change alone. It must be associated with other substances such as carbon dioxide, acids, alkalies, or perhaps bacteria. It is the effect of a combination of these causes that produces the harmful results observed in metals used for various purposes.

The simplest method of effecting corrosion is by means of chemical solution, that is the metal merely dissolves in the corroding liquid; for example,

the solution of iron in hydrochloric acid. The process may be more complicated, as when it is due to the combined influences of different elements. When brass is exposed alternately to sea water and the atmosphere, the corrosion is due to the solvent action of the water and the subsequent oxidation of the copper to the oxychloride. Then again the electrochemical method of corrosion is very common and occurs when two metals, with different electrochemical properties, are in contact under a conducting liquid. A galvanic couple is formed and the solution of one of the bodies follows. This may take place between different metals or within the same metal or alloy, if the structure is not homogeneous. Thus it is that alloys formimg solid solutions are more resistant to corrosion than those whose parts separate out on cooling. The presence of dross, oxides and other impurities having conductivity have the same effect of acceleration.

Corrosion may stop automatically by the formation of insolule films upon the surface as is the case with lead. The use of lead for the conveying of water would not be possible owing to the amounts of the metal dissolved but for the fact that a coatimg of lead sulphate is soon formed which prevents any further action.(65) A similar phenomenon is observed in the case of any alloy of 50 o/o gold and 50 o/o silver. This alloy is neither soluble in nitric nor hydrochloric acid. The silver chloride formed in the presence of the hydrochloric acid prevents the dissolving of the silver below it and the gold itself is not soluble, and again, the gold remaining after the silver is dissolved away by the nitric acid protects the remaining gold from the acid. Some alloys of copper behave in the same way.

In order to understand the present status of the question of the causes and prevention of corrosion it is necessary to take a review of the literature, much of which is conflicting , and draw our conclusions from the results as found by many investigators. In order to do this the references pertaining

to the different metals have been collected and arranged under their respective heads.

IRON. Owing to the economic importance of iron it is not surprising that a larger amount of work has been done upon it than upon any other metal to prevent its deterioration and to lengthen its useful life. The fact that moisture and oxygen are necessary to its rusting has been agreed upon by all investigators. Just how this change is effected is still, however, an open question. There have been three theories advanced to explain the mechanism of rusting, the carbonic acid, the hydrogen peroxide and the electrolytic theories.

THE CARBONIC ACID THEORY.

The carbonic acid theory was advanced by Crace Calvert(67) and has been till lately the one most generally held to explain the phenomenon of rusting and takes for its basis the assumtpion that iron to rust requires the presence of carbonic acid or some other acid. The theory asserts that the process of rusting is explained by the following equations:

$$2Fe + 2H_2CO_3 = 2FeCO_3 + 2H_2$$

$$2FeCO_3 + 5H_2O = 2Fe(OH)_3 + 2H_2CO_3$$

From the equations it is seen that the process is a cyclical one; the iron first being changed to ferrous carbonate by the carbonic acid and the ferrous carbonate further changed to ferric hydroxide by the action of oxygen and water and the liberation of carbonic acid: the carbonic acid then being capable of repeating the process. Moody is a strong supporter of this theory and insists that in the absence of carbonic acid iron cannot rust. He has been able to place iron in contact with oxygen and water for many weeks without the slightest trace of rust appearing upon the (20)

surface. His method of proceedure was to immerse the iron in chromium tri-oxide, in a bent tube, and after passing air through for three weeks distilled water was boiled in a flask connected with the tube containing the iron and the iron thus washed free from the chromium tri-oxide and exposing the sample to the action of oxygen and moisture. When this method was followed no action occured. 56.2 L. of air were passed over the iron in this way or thirty times enough oxygen to completely oxidize the sample. When carbon dioxide was passed through the apparatus rusting began in a short time and in a few hours the surface was distinctly tarnished. From this experiment Moody concluded that without the presence of carbon dioxide iron is unable to rust. The amount of oxygen absorbed by iron is greatly influenced by carbon dioxide. This is shown in the following table prepared by Moody.

	Per cent. of total oxygen absorbed by 10 gms. of iron from 100 cc. of air.	
	Ordinary air and distilled water.	Air and water almost free from CO_2.
After 6 hrs. exposure	5.7	none
" 24 " "	29.1	none
" 72 " "	61.3	0.9
" 168 " "	94.3	3.8

It has been found that iron rust varies in its composition and that when exposed to the air undergoes a change from the ferrous to the ferric condition as much as 18 o/o of ferrous oxide being changed to ferric oxide and 5 o/o from ferrous carbonate to ferric carbonate. Moody speaks of the constant liberation of hydrogen from the surface of iron and thus accounts for the persistance of iron in the ferrous condition as rust. The composition of iron is altogether out of harmony with the hydrogen peroxide theory, and if hydrogen peroxide were formed in the ratio as stated by the supporters of

the theory, ferrous oxide and ferrous carbonate could not be formed in rust, for both these subatances are oxidized by hydrogen peroxide. The only way of accounting for the presence of these substances in rust is to suppose that they are formed in the early stages of atmospheric corrosion by the action of carbon dioxide, the metal forming the ferrous carbonate and the subsequent loss of carbonic acid.

An experiment described by Moody in which he determined the influence of carbonic acid in dissolving iron is in direct contradiction to the results of Dunstan and is as follows: "Distilled water which has been shaken with or left in contact with air is poured on a perfectly clean, polished surface of iron. At the end of 40 sec., when the water is seen to be clear and the metal perfectly bright, the water is all allowed to run into a porcelain basin containing a drop of a dilute solution of potassium ferricyanide. A marked blue color results. If a similar experiment be made with rain water instead of distilled water, the iron is found to be even more readily attacked, ferrous salt in solution being detected after 30 sec. contact. The ferrous iron found in solution in these experiments is obviously formed by the interaction of a very dilute solution of carbonic acid and iron, for recently boiled distilled water does not dissolve the metal. "Clear borings of iron were kept in water which was kept saturated with carbonic acid at ordinary temperature and pressure. Hydrogen was steadily evolved from the surface and provided air was excluded the solution remained clear".

(20) P725.

(Table showing amount of iron dissolved by CO_2 expressed as FeO per L.)

After 20 hrs.	contact-	0.2546	gms. of FeO per L.
" 30 "	"	0.3771	" " " " "
" 56 "	"	0.5245	" " " " "
" 96 "	"	0.8172	" " " " "
" 26 days	"	2.1390	" " " " "

It has been a generally accepted belief that alkali will prevent the rusting of iron but no work of any importance was done upon the subject until C.H.Cribb took up the investigation.(22) He used varying amounts of alkali, different alkalies and varying temperatures. His results seem to show conclus - ively that iron does rust in the presence of alkaline solutions up to a certain concentration. Cribb used sodium hydroxide, calcium hydroxide, sodium carbonate, barium hydroxide and ammonium hydroxide, in his experiments and found that the action is at first general with weak solutions of alkali becoming more and more localized as the concentration increases and the action suddenly ceasing altogether. He has given no satisfactory explanation of this strange phenomonen. The amount of iron rusted is not in proportion to the area attacked, the amounts of magnetic oxide being practically the same when the action was localized.

HYDROGEN PEROXIDE THEORY.

This theory advanced by Dunstan, Jougtt and Goulding is that iron cannot rust unless hydrogen peroxide is formed in the process. They cite the fact that iron is not rusted in the presence of alkaline solutions as a proof of their theory. Hydrogen peroxide is unstable in alkaline solution and the iron does not rust because of the absence of hydrogen peroxide. The soluble salts of chromic acid and the acid itself inhibit the corrosion of iron and also destroy hydrogen peroxide. This fact has been pointed out also as a strong proof in favor of the peroxide theory. The equations involved should be written:

$$Fe + O_2 + H_2O = FeO + H_2O_2$$

$$2FeO + H_2O_2 = Fe_2O_2(OH)_2$$

Tests for hydrogen peroxide have been obtained during the slow oxidation of zinc but no trace has been found during the rusting of iron. Hoppe Seyler

has explained the formation of hydrogen peroxide in the corrosion of metals as an oxidation process, the substance being oxidized by one atom of a molecule of oxygen, the other atom attaching itself to a molecule of water forming hydrogen peroxide.

$$Fe + O_2 + H_2O = FeO + H_2O_2$$

Another explanation is that the oxygen is not taken from the molecular state but is taken from water: the hydrogen then uniting with one molecule of oxygen to form hydrogen peroxide.

$$Fe + OH_2 + O_2 = FeO + H_2O_2$$

The hydrogen peroxide in this case would not be oxidized water but reduced oxygen.

The explanation given to rusting by Dunstan, Jouett and Goulding is supported by experimental evidence. They recognize that there may be three factors involved:(1) the direct oxidation process which depends on the action of iron and oxygen together with liquid water;(2) the action of atmospheric carbon dioxide and(3)electrolytic action generated by impurity. These investigators have conducted a series of experiments that it is well to review. They throw considerable light on this much discussed question. The first experiment was to determine the action of moist and dry gases upon iron. Samples of very pure iron (99.94 o/o) were placed in oxygen, carbon dioxide, a mixture of carbon dioxide and oxygen, a mixture of oxygen and ammonia. The gases in one set were dried and in the other were saturated with water vapor. The iron sample, after polishing, was placed in a piece of hard glass tubing and sealed at one end; the tube heated to redness and a stream of hydrogen passed over it. The other end of the tube was then sealed and the iron allowed to cool in the atmosphere of hydrogen. The results of these experiments are as follows:

	Constant temp.	Variable temp.
Dry gases	No visible action	No action
Moist oxygen	"	Large amt. of rust formed.
Moist oxygen and carbon dioxide	"	Copious rusting
Moist oxygen and ammonia	"	No action
Moist carbon dioxide	"	"

The investigators considered that it proved that rusting does not occur in the presence of either dry or moist oxygen, carbon dioxide or, if the temperature is constant, in a mixture of these gases. C. Calvert found that carbon dioxide and moisture formed iron carbonate, pure oxygen, carbon dioxide and moisture caused rusting rapidly while pure oxygen and moisture did not rust iron at all. These results are at variance with the results above. The experiments of Dunstan, Jouett and Goulding lead to the following conclusions: in the case of oxygen and carbon dioxide in a moist condition, no rusting occurs as long as the temperature is constant, if the temperature changes water condenses on the surface and rusting occurs. It was found that iron when left in contact with water saturated with hydrogen and in a hydrogen atmosphere showed no visible action, when oxygen was admitted, however, rusting began at once. Nitrogen was substituted for hydrogen with the same results. The solubility of iron in water was also tried with the result that no trace of iron could be found, even with the most refined methods. The experiments of Whitney were repeated without result. By the method of the experiment, two pieces of iron were inclosed in a glass vessel when the distilled water was still boiling. The two samples were of purified iron, each of 1-1/2 inch square. The stopper carried a glass tube projecting 7 to 8 inches and ending in a capillary. The water was kept boiling and the capillary sealed and the stopper sealed with paraffin wax. The flask remained closed for three weeks with-

out visible action. It was then opened and one half the liquid poured out into a beaker. The liquid in the beaker showed no sign of rust appearing on open exposure to the air while the water containing the iron rusted in the usual manner after about one hour. No test for iron could be obtained in the liquid poured off from the iron. It is assumed then that it is proven that iron rusts without the aid of carbon dioxide and that the inhibitive action of alkalies on the process of rusting must have some other explanation than that the alkali removes the carbon dioxide. Sodium carbonate, potassium carbonate, ammonium carbonate, ammonia, calcium hydroxide, borax, disodium, hydrogen phosphate, sodium nitrite, potassium ferrocyanide, chromic acid, potassium chromate and potassium dichromate, in moderate dilution, prevent the rusting of iron even after years of exposure to the solution. Iron covered with platinum black, manganese dioxide, lead hydroxide or pure animal charcoal prevents the rusting of iron, in most cases and always slows the reaction down greatly. Calcium carbonate, however, seems to have no effect upon the oxidation. The protective action of insoluble compounds depends, to a great extent, upon the nature of the precipitate, its composition, and its method of precipitation. The supporters of this theory found that the following salts did not prevent the corrosion of iron; sodium chloride, potassium chlorate, ferrous sulphate, potassium nitrate, potassium ferricyanide, and sodium sulphate. The assertion is made that these substances that prevent the corrosion of iron are also antagonistic to the formation of hydrogen peroxide. Hydrogen peroxide has been found where certain metals are oxidized by the action of air, for example, zinc. No trace of it have been found in a solution in which iron is undergoing oxidation, however. (A very significant fact, it seems.) In order to test for hydrogen peroxide the investigators used freshly reduced iron and the sample shaken with oxygen and water. The

solution on examination showed no trace of hydrogen peroxide by the titanic acid method. On treating zinc under the same conditions a positive test for hydrogen peroxide can be obtained. Iron placed in a soltuion of hyrdogen peroxide rusts at once and since zinc attacks it so vigorously it would be a difficult matter to detect hydrogen peroxide in a solution containing rusting iron. Hydrogen peroxide was added to a solution of borax and lime, respectively, in which was placed a sample of iron. The iron was unattacked but the hydrogen peroxide was decomposed with the liberation of oxygen. Iron in a strongly alkaline solution of hydrogen peroxide decomposes the peroxide rapidly and oxygen bubbles are liberated upon the surface but no rusting occurs.

It has been found that, in general, those metals which rust in air are oxidized by hydrogen peroxide and those metals which are not oxidized by it are not rusted in the air. The members of the first class are: Fe, Zn, Cd, Pb, Al and Bi; second class,Cu, Pt, Ag, Au, Ni and Sb.Without exception the metals of the first class are stopped in their oxidation by those substances which decompose hydrogen peroxide. Carbon dioxide plays an unimportant part in the corrosion of iron and is in no way necessary to the formation of rust. Further experiments were carried out by these workers to determine the part played exactly by carbon dioxide. A saturated solution of carbon dioxide was produced by passing purified gas (HCL - $CaCO_3$) into distilled water, freshly boiled. Sodium hydrogen carbonate was used to purify the carbon dioxide. Four flasks were used, A, B, C, D.

A. 100 cc. carbon dioxide solution - carbon dioxide gas - pure iron.

B. 50 cc. carbon dioxide solution - 50 cc. well boiled water - 3 pieces of iron. Atmosphere of air above the liquid.

C. 10 cc. carbon dioxide solution - 90 cc. air free distilled water

with atmosphere of air.

D. 100 cc. air free water - three pieces of iron, atmosphere of air. After ten to fifteen minutes the surface of (A) was thickly coated with bubbles. (B) Surface covered with bubbles of a smaller size. (C) Bubbles very small. (D) No bubbles at all. After 19 hours the solution in (A) was clear and colorless, the surface of the metal still remaining coated with bubbles. (B) The solution was faintly yellow and opalescent; only a trace of iron appearing where the bubbles were present. (C) Liquid pale in color, a small amount of reddish brown rust throughout the solution, more rust than in (B) was observed. (D) Thickly coated with rust in the usual manner. The iron dissolved was determined in each case.

A.	B.	C.	D.
0.005.	0.004	0.0022	0.0012.

These experoments show that carbon dioxide and water are capable of dissolving iron, even in the absence of oxygen. It has been shown that iron will rust in the absence of carbon dioxide, hence the minute quantity of carbon dioxide in the air is a small factor in the process of rusting. Dunstan, Jouett, and Goulding were unable to obtain hydrogen from rusting iron and hence concluded that the electrolysis theory could not be held for the ordinary corrosion of iron.

ELECTROLYTIC THEORY.

In order to explain many facts in chemistry and physics the theory of electrolytic dissociation has been advanced. By its aid we are able to explain the electrical conductivity of salts dissolved in water, abnormal osmotic pressure, the lowering of freezing point,etc. When a salt dissolves in water a certain portion of it is dissociated or its molecules are broken up by the water into parts, called ions. These parts of molecules may be made up of a single atom or groups of atoms but they differ from real atoms in

that they carry a large charge of electricity. For example: when salt is dissolved in water the salt is broken up into two parts, the positive sodium and the negative chlorine, each carrying a charge of positive and negative electricity respectively. Water is to some extent ionized. This is an important fact in the theory for the rusting of iron electrolytically.

When any substance, such as a metal, is put into a solution there is a tendency to pass into solution. This tendency varies with different substances the pressure of iron being about 10,000 atmospheres. This tendency to pass into solution is called "solution pressure". The portion of the metal that passes into solution becomes positive and the metal from which it is dissolved becomes negative. This dissolving action will continue just so long as the electrolytic tension is not larger than the solution pressure. If in this solution there be another metallic ion with a less solution pressure it will tend to pass back to the metallic state plating upon the first metal. The solution around the first metal upon which the plating is taking place will be negative and the metal itself positive. The result is that when the second metal passes back into the metallic state, and, in plating out, a current of electricity will pass from the solution, through the metal across to the second metal, or the place from which the metallic ions are being discharged and back through the solution to the starting point. This is illustrated in the ordinary wet cell. A metal may have a tendency to dissolve yet not be oxidized in solution. There must be another metal in electric connection to act as an electrode and this electrode must have a lower solution pressure than the iron. Copper will cause the dissolving because its electrolytic solution pressure is less than iron, zinc on the other hand will prevent the solution of iron. Hydrogen is classed electrochemically with copper and if a cell were constructed with hydrogen replacing copper and iron in place of zinc a current would flow and hydrogen be deposited on the iron, the

iron going into solution, the velocity of the reaction being proportional to the external resistance. The same thing happens when iron dissolves in water. The water is dissociated into hydrogen and hydroxal ions. Hydrogen has a less solution pressure than iron and hence the hydrogen is deposited upon the iron and the hydroxal ions are left to neutralize the positive ion of iron. An electric current flows from the iron by means of the metallic ions in solution and back by means of the hydrogen ions. The hydrogen deposited upon the iron is not a good conductor of electricity and polarization is quickly effected and the solution of the iron ceases. In order that the action proceed the hydrogen ions must be removed from the iron. This is the function of the oxygen in solution, combining with the hydrogen forming water, and the solvent action continues. It was formerly thought that the function of the oxygen was to oxidixe the iron ions in solution and precipitate rust; this is true, but it is only a secondary function of the oxygen. The speed of the reaction is directly proportional to the number of hydrogen ions present. If an acid is added; for example, carbonic acid, the solution of the iron should be increased and this is just what happens. When a great enough concentration of hydrogen ions is reached, as when a strong solution of a mineral acid is added; the hydrogen is given off in greater quanity, and as gas, from the surface of the iron.

Dr. Friend (Carnegie Research Scholar) has conducted experiments from which he concludes that when pure iron is placed in pure water, free from carbon dioxide and oxygen, no iron is dissolved, using potassium sulphocyanate as a test for iron ions, but when a minute quanity of carbonate is present - that adhering to the sample and the sides of the vessel - iron is dissolved and a percipitate of rust formed. He concludes: "We thus see that the electrolytic theory of corrosion is untenable".

Pure water is dissociated to the extent of 1 gm. of H in10,000,000 L. If iron were dependent upon the hydrogen ion content in water for its solution the action would be very slow. Water is slightly an acid and to this extent will dissolve a metal. If hydrogen ions are increased in any way the action is mush more rapid. Just how far the action will go is dependent upon the compounds formed after solution. If the substances formed after oxidation are insoluble and are not removed the action of solution is slow and continues only with great difficulty and if on the otherhand the products are removed the action of solution is much more rapid and continues with a bright surface exposed. The equation that probably represents the action of water upon iron is:

$$3Fe - 4H_2O = Fe_3O_4 - 4H_2$$

Deville found that the lower the temperature the greater was the tendency for iron to oxidize. It is thus easily seen that at ordinary temperatures iron in contact with water will generate hydrogen. Faraday has shown that electrolysis will take place in solutions even after all visible action has ceased. He attributes this feeble current to the metallic conduction of the solution. Hemlholtz has shown that the electrolysis is due to the solution of the substance just as when iron dissolves in copper sulphate. If it is true that the rate of solution is dependent upon the concentration of the hydrogen ion then anything which reduces the concentration will retard the solution. The product of the concentration of the hydrogen and the hydroxal ions is a constant. For water this constant is 10^{-7}. If the hydroxal ions are increased the hydrogen ions must be diminished so that the product will remain constant. If an alkali is added this result is obtained and the corrosion will be diminished. This is really the case and many practical applications are made of it. Steel tools and iron in the process of manufacture are kept in a solution of lime. Lime compounds are used in steam boilers to

diminish the corrosion and many other practical applications. It is a fact that the neutral salts of calcium do not behave in the same way and hence the phenomenon can be attributed to the hydroxal ions only. Other soluble alkalies act equally well. Compounds such as NH_4CL and $MgCl_2$ increase the hydrogen content and must be guarded against in boiler water where they are subject to pressure. Another valuable function of alkali in boiler water is the dissolving of the CO_2 contained in the feed water. The tendency of the CO_2 is to collect in the cooler parts of the system and there set up a dissolving center from the fact of the increased number of hydrogen ions. This action is found in return pipes in heating systems and it is in these pipes that the greatest corrosion occurs. W. R. Whitney gives the results of his experiments on this point. He foumd that the action of CO_2 was cyclic, the same acid repeating its action indefinitely. (19) P402.

"Let us imagine a steam heating system made up of a boiler with steam pipes leading to various stacks and radiators from which return pipes, bringing the condensed steam back to the boiler, enter below the water line. For simplicity we assume that the plant is run without the addition of water after the boiler has been originally charged. In other words no steam is blown out into the air, and the plant is not used as some are, to incidentally supply hot water for foreign uses which thus requires a continual water feed. Our closed system usually contains, when in actual running condition, a number of dead-ends where gases have accumulated and the pipes are cold. This may be observed in radiators of common type. Into this cooler part of the system such gases as, oxygen, nitrogen and carbonic acid, which were originally in the feed water, will collect. Here they will dissolve in the condensed water which is to return to the boiler, the CO_2 being especially soluble. The carbonic acid or its active hydrogen will cause the solution of iron from the

return pipes and this iron will be carried back towards the boiler as bicarbonate of iron, being held in solution just as is calcium carbonate in water containing carbonic acid. This may be represented by the equation:

$$Fe + 2CO_2 + 2H_2O = H_2Fe(CO_3) + H_2$$

In the case of the bicarbonate of calcium solution it is well known that boiling it decomposes the salt and liberates half the carbonic acid leaving a precipitate of calcium carbonate. In the case of the soluble carbonate of iron, as will be shown, the decomposition of the compound by heat liberates all the carbonic acid instead of half of it and produces the insoluble oxide or hydroxide of iron. Whether this decomposition of the soluble iron takes place in the boiler after the solution has returned to it, or in the return pipe where the promixity to the boiler produces a sufficiently high temperature is of no immediate importance. In either case the carbonic acid is all set free and must return with the steam to the cooler parts of the system; there again it will dissolve in the condensate, again render soluble some iron and carry it toward the boiler and so forth. In each cycle of this kind hydrogen will be set free which will remain in the cooler parts of the system, as it is but slightly soluble in water. It seems necessary, therefore, that in common practice a very small quanity of carbonic acid must often cause an unlimited amount of corrosion without in any way loosing its power to continue the process. The process of the corrosion in this case will amount in "toto" to the union of iron with oxygen of water and the liberation of hydrogen, the carbonic acid acting merely as a catalyzer, where the mechanics of its action is apparent. This peculiar condition of affairs has been observed by us in certain large heating plants where we have found, first the carbonic acid in the feed water, secondly, much carbonic acid mixed with hydrogen, nitrogen and oxygen in the dead-ends or cool parts of the system; thirdly, water in the return pipes in

which rapid corrosion of the pipeing was taking place, in which much dissolved bicarbonate of iron was found; and finally much precipitated oxide of iron in the boiler and hottest part of the return pipes". Laboratory experiments have also been conducted which show the same results as those described by W. R. Whitney above.

A reagent has been devised by Wm. H. Walker and A. S. Cushman termed "Ferroxyl" which shows that iron is dissolved at different points with different velocities and with the formation of basic and acid ions. It shows this much, at least, and will be discussed later. Ferroxyl is a dilute solution of phenolphthalein and potasium ferricyanide thickened with gelatine to prevent convection currents. There is formed a bright blue color where the iron is going into solution and a bright red color at those portions where the hydrogen is being deposited, leaving the hydroxal ions behind. This color picture is easily obtainable with an ordinary iron nail, being sure that all alkali is removed. The flow of the current as indicated is from the ends of the nail as in the case of magnetic lines of force. In order to show that the principle function of the oxygen is to depolarize the iron experiments are given by W. A. Walker (68). If a piece of iron is placed in ordinary water exposed to the air it will rust. If a piece of platinum is placed in the water no difference is observed. The oxygen is still present in the solution as it was before and the iron is being oxidized and precipitated as it dissolves. If the platinum and iron are connected electrically an increase in the corrosion of the iron is observed. There has been no change in the solution chemically but the change lies in the fact that when the platinum and the iron are connected the platinum furnishes a surface upon which the hydrogen can deposit and acts as a catalyser, causing the hydrogen to be taken from the solution by the oxygen. If into a U tube containing a weak electrolyte two pieces of electrically connected iron are put, one in each arm, and the bottom of the U

between them plugged with jelly and the solution, protected from the air, no action will be observed . The iron will tend to go into solution in this system but will be prevented from doing so by the film of hydrogen that will attach itself to the surface of the iron and owing to the high resistance no current will pass through the system. If in one of the limbs there be placed a substance that will unite with hydrogen, such as hydroxylamine, no action will be observed in that side but the iron in the other limb will dissolve and at the same time current will flow through the whole system.

An other example is the action of an electrolyte upon zinc. In a weak salt solution containing a rod of zinc and one of iron, the iron will pass into solution and the zinc will hardly be attacked. If the metals instead of being seperated are connected the iron is arrested in its corrosion and the zinc passes into solution. The explanation for this has been that the zinc formed a film upon itself of oxide or hydroxide that protected it from solution. This explanation in not tenable since the contact of the two metals cannot effect this coating. The solution of the question from the electrolytic theory is that in the first case there is no action because the zinc surface does not catalyse the reaction: $H_2 - O = H_2O$ rapidly enough to remove the hydrogen from the surface. The hydrogen there protects the zinc from solution. The catalysing action of the iron is strong enough to cause the formation of water upon the surface and hence its solution. The solution preasure of zinc is stronger than that of iron, the zinc should therefore pass into solution but it does not. The reason for this is that the electrolytic double layer set up on the surface is not so easily destroyed by a flow of an electric current. If the two metals are connected the high solution pressure of the zinc forces the zinc ions into solution and the metal itself becomes an anode, the iron cathode, and no more iron is dissolved: the cathode forming a surface upon which hydrogen may be deposited that has been set free by the solution.

EXPERIMENTAL.

It is evident from the previous discussion that the experimental data vary greatly upon important points in regard to determining the manner in which iron rusts. Some of the work of different investigators has been repeated by the author in order to decide upon the truth of the various results as reported. The questions at issue are: (1) is iron soluble in pure water away from the influence of carbon dioxide and oxygen, (2) the power of alkaline solutions to inhibit corrosion, (3) the effect of carbon dioxide and oxygen upon the corrosion of iron,(4) the relative rate of corrosion of different kinds of iron.

A sample of pure iron was used in determining the action of pure water upon its solubility (99.8 o/o). The surafce of the sample was carefully polished, first on an emery wheel, then on an oil stone and lastly with 00 emery paper. (All samples were given the same treatment.) At no time after polishing was the iron touched with the fingers. The sample was placed in 100 cc. of boiling distilled water free from carbon dioxide into which a stream of hydrogen was being passed. This operation was continued for 1 hour, at the end of which time the flask was sealed at (A) and (B) Fig. 1 and further sealed at the stopper with paraffin to prevent leakage of air.

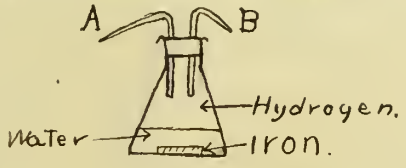

Fig. I.

The flask was thus left sealed for four days in water free from carbon dioxide and oxygen and in an atmosphere of hydrogen. At the end of the four days the 100 cc. of water was evaporated to 10 cc. in a platinum dish and tested for iron with potassium sulphocyanate. A marked test for iron was obtained showing that iron is dissolved in pure water without the action of carbon dioxide

and oxygen.

Into five Erlenmeyer flasks, 200 cc. capacity, A, B, C, D, E were put the following:

(A) 100 cc. boiled distilled water, 0.25 cc. N/10 KOH, phenolphthalein and one sample of iron (2 x 1 x 1/8).

(B) 100 cc. boiled distilled water, 0.5 cc. N/10 KOH, phenolphthalein, and sample of iron. (All samples were of the same size as above).

(C) 100 cc. boiled distilled water, 1 cc. N/10 KOH, phenolphthalein, and sample of iron.

(D) 100 cc. boiled distilled water, 2.5 cc. N/10 KOH, phenolphthalein, and sample of iron.

(E) 100 cc. boiled distilled water, 5 cc. N/10 KOH, phenolphthalein, and sample of iron.

The iron used in all of the flasks was of the same kind with a purity of 99.8 o/o iron. Rusting began after 3 hours in (A) and (B); 5 hours in (C) and 8 hours in (D). There was a gradual graduation of corrosion from (A) to (D) being greatest in (A). The color of the indicator was different in all of the solutions being a light brown in (A), light pink in (B) and shading to dark lavender in (E). The results are shown in the following table. (Table I). An experiment was carried out to determine the effect of carbon dioxide upon the corrosion of iron. Four samples were used in this experiment, "muntal metal", "woods metal", charcoal iron and pure iron.

In the first test the four samples were immersed in distilled water and a current of air passed through for fourteen days; the loss in weight being determined at the end of that time. In the second test the samples were immersed as before but carbon dioxide was substituted for air. In both experiments the water was open to the air. The results are shown in tables 2 and 3. The relative rates of corrosion of the four different kinds of iron is also

shown in tables 2 and 3.

It has been shown that iron can rust without the presence of carbon dioxide and that iron does not rust in the presence of some substances which do not decompose hydrogen peroxide. The carbonic acid theory and the hydrogen peroxide theory do not, therefore, seem to be tenable as an explanation for the corrosion.

Let us turn our attention to the electrolytic theory of corrosion. In order to explain the phenonomen in this way hydrogen ions must be in solution. If it is necessary that hydrogen ions be in solution when iron under goes corrosion we would expect iron to remain bright in an alkaline solution. It has been shown that there is a concentration of alkali below which iron will corrode. This fact seems to be in direct contradiction to the electrolytic theory as explained by Cushman. (24) P. 24.

"Reduced to its simplest terms, the following explanation of the rusting and corrosion of iron seems to the writer the only one that is tenable. In order that rust should be formed iron must go into solution and hydrogen must be given off in the presence of oxygen or certain oxidizing agents. This presumes electrolytic action, as every ion that appears at a certain spot demands the disappearance of a hydrogen at another, with a subsequent formation of gaseous hydrogen. The gaseous hydrogen is rarely visible in the process of rusting owing to the rather high solubility and great diffusive power of this element. Substances which increase the concentration of the hydrogen ion, such as acids and acid salts, stimulate corrosion, while substances which increase the concentration of the hydroxal ion inhibit it. Chromic acid and its salts inhibit corrosion by producing a polarizing or dampening effect which prevents the solution of iron and the separation of hydrogen."

While it is true that iron does go into solution in pure water and that positive and negative points are developed on the surface of iron, as is shown

by the "ferroxyl" reagent, the fact that iron does rust in alkaline solution is not explained by this theory. (27) P 25.

CONCLUSIONS.

1. Iron can rust without the presence of carbonic acid.
2. Iron is soluble in pure water away from the presence of carbonic acid and oxygen.
3. Iron will rust in alkaline solution up to a certain concentration of the alkali.
4. Pure iron is more resistant to corrosion than impure iron.
5. The addition of silicon to aluminum increases its solubility in acids.
6. The rate of solution of pure iron increases as the time of solution.
7. The testing of the relative rate of corrosion of alloys by means of their solubility in acids is unreliable.
8. That carbon dioxide may take part in the corrosion of iron is not questioned but it is not essential to the formation of rust. That electrolysis is often the cause of corrosion is evident from experiment but it seems that some other factor, not as yet known, is responsible for some forms of corrosion that cannot be explained by any theory existing at present.

The acids used in all experiments were composed of 1 part concentrated acid and three parts water.

The purity of iron in all cases in which "pure iron" was used was 99.80 o/o. Manufactured by American Rolling Mill Company, Middletown, Ohio, Trade name "American Ingot iron".

"Woods Metal" is the ordinary sheet iron used.

"Muntal Metal" is a pure grade of iron used for eaves and gutters on houses.

Four Day Experiment with Distilled H_2O to which KOH had been added.

C.C. N/10 Solution KOH per 100 cc H_2O.	Alkali by weight in 100000 Vol H_2O	Temp.	Area and Nature of Action.	C.C. KOH distroyed by action.
0.25	1.4	25°C	Long thin streaks extended transversely across plate.	0.02
0.50	2.8	" "	Thin streaks less than above.	0.20
1.0	5.6	" "	Few streaks but small round patches.	0.034
2.5	14.0	" "	One small patch.	0.27
3.0	28.0	" "	No. action.	0.11

Table. No. 1.

R. J. Howard '10

TABLE SHOWING RELATIVE RATES OF CORROSION OF "WOODS METAL," MUNTAL METAL, CHARCOAL IRON, AND PORE IRON IN DISTILLED WATER AND TAP WATER.-

SAMPLE	REAGENT.	TEMP.	TIME	WT TAKEN	WT DISSOLVED	PER. CENT DISSOLVED.	AVE % DISSOLVED.	REMARKS.
"Wood's Metal"	ORDINARY AIR BUBBLED THROUGH DISSTILLED WATER.	25° C	14 DYS.	35.4	2.3 GRMS	6.49	6.18	THE AREA EXPOSED OF ALL EXAMPLES WAS 25 ^{cm}" THE PER CENT IRON DISSOLVED BY WEIGHT IS NOT INDICATIVE OF THE RELATIVE RATE OF CORROSION. THE DISTILLED WATER CONTAINED LARGE AMOUNTS OF CARBONIC ACID.
		" "	" "	35.7	2.1	5.88		
"Muntal Metal"		" "	" "	36.7	1.6	4.36	4.55	
		" "	" "	35.8	1.7	4.75		
Pipe C. Coal Iron.		" "	" "	220.0	1.95	0.886	0.914	
		" "	" "	222.6	2.10	0.943		
Pore Iron.		" "	" "	91.5	1.4	1.53	1.59	
		" "	" "	84.6	1.4	1.65		
"Wood's Metal"	ORDINARY AIR BUBBLED THROUGH TAP WATER.	" "	" "	33.4	2.15	6.44	6.27	THE AREA EXPOSED OF ALL SAMPLES AS 25 ^{cm}" THE WATER WAS HIGH IN IRON AND CARBONATES
		" "	" "	33.6	2.05	6.10		
"Muntal Metal"		" "	" "	35.1	1.60	4.56	4.18	
		" "	" "	34.1	1.30	3.81		
Pipe C. Coal Iron.		" "	" "	221.6	1.60	0.724	0.929	
		" "	" "	224.7	2.10	0.935		
Pore Iron.		" "	" "	90.10	0.9	1.01	1.35	
		" "	" "	93.20	1.4	1.68		

TABLE No 2

R. S. HOWARD '10.

TABLE SHOWING RELATIVE CORRISION OF WOOD'S METAL, MUNTAL METAL, CHARCOAL IRON AND FORGE IRON IN H_2O SATURATED WITH CARBON DIOXIDE.

SAMPLE.	REAGENT	TEMP.	TIME.	WT. TAKEN.	WT. DISSOLVED	PER. CENT DISSOLVED	AVERAGE % DISSOLVED.
CHARCOAL IRON.	CARBON DIOXIDE BUBBLED THRU DISTILED H_2O	85°C	14 DYS.	218.05	1.60	0.73	0.61
		" "	" "	220.50	1.10	0.53	
MUNTAL METAL.		" "	" "	33.50	1.30	3.88	4.74
		" "	" "	32.80	1.84	5.61	
WOOD'S METAL.		" "	" "	31.25	1.59	5.10	5.09
		" "	" "	31.55	1.60	5.08	
FORGE IRON.		" "	" "	89.20	1.30	1.68	1.47
		" "	" "	81.80	1.03	1.26	

TABLE NO. 5

R. D. HOWARD '10

TABLE SHOWING RELATIVE SOLUBILITUAL OF TWO SAMPLES OF APROX PURE IRON.

SAMPLE	ACID.	TEMP.	TIME.	WT. TAKEN.	WT. DISSOLVED.	PER. CENT. DISSOLVED.	AVE % DISSOLVED	REMARKS.
APROX. PURE IRON.	HNO_3	25°C To 70°C	72 Hrs.	7.9479	7.9479	100.00	100.00	THE FOLLOWING RATIOS SHOW THAT RATE OF SOLUTION INCREASE, AS THE TIME.
				8.2109	8.2109	100.00		
	HCL	" "	" "	8.0443	.4178	5.18	5.165	1.37 : 5.16 = 1 : 3.80 24 Hrs. - 72 Hrs.
				8.2255	.4338	5.15		
	H_2SO_4	" "	" "	8.2300	.8161	9.91	9.82	2.40 : 9.82 = 1 : 4.09 24 Hrs. - 72 Hrs.
				7.9987	.7758	9.73		
APROX. PURE IRON.	HNO_3	25°C To 75.5°C	24 Hrs.	8.6449	8.6448	100.00	100.00	
				8.1223	8.1223	100.00		
	HCL	" "	" "	8.1905	.1213	1.48	1.37	
				8.5017	.1079	1.26		
	H_2SO_4	" "	" "	8.3773	.2012	2.41	2.405	
				8.2903	.1993	2.40		

TABLE NO 4

JOLUBILITY OF ALLOY CONTAINING - NI. - CR. AND TRACE OF AL.

SAMPLE.	ACID	TIME	WT. TAKEN.	WT. DISSOLVED	PER. CENT. DISSOLVED	REMARKS-
CAST BAR. 2. NI. 90% CR. 10% AL - TRACES	HNO_3	HRS 24	3.1494	.2147	7.94	THIS SAMPLE WAS SOFTER THAN BAR. 4.
			3.0081	.2721		
	HCL	" "	3.5207	.0037	.114	
			2.7888	.0035		
	H_2SO_4	" "	2.2000	.0015	.055	
			1.4393	.0006		
DUPLICATE ON SAMPLE ABOVE.	HNO_3	" "	2.9347	.00	7.82	ALL TESTS WERE CARRIED OUT UNDER SIMILAR CONDITIONS- THIS ILLUSTRATES AGAIN THE UNUNIFORMITY OF RESULTS OBTAINED BY DISSOLVING ALLOYS IN ACIDS-
			2.7360	.2026		
	HCL	" "	3.5260	.0040	.204	
			2.7853	.0082		
	H_2SO_4	" "	2.1985	.0006	.020	
			1.4387	.0002		
TRIPLICATE ON SAMPLE ABOVE.	HNO_3	" "	2.6960	.7652	28.47	
			2.5339	.7493		
	HCL	" "	3.5220	.0117	.332	
			2.7771	.0097		
	H_2SO_4	" "	2.1979	.0024	.109	
			1.4385	.0012		

TABLE NO 5

E. S. HOWARD.

Relative Solution of Alloys Containing Ce.-Al.- and Ni. in Acids.

Sample	Acid.	Temp.	Time.	Wt. Taken	Wt. Dissolved.	Per. Cent. Dissolved	Remarks.
Bar 4. Ce.-20% Al.-10% Ni.-79% Hard, brittle, very fine grained.	HNO_3	25°C	24 Hrs.	5.2043	.1277	1.37	The metal in the nitric acid did not behave uniformly. One solution was very highly colored and the other was not.
				5.0779	.0147		
	HCl	"	"	4.3703	.0084	.174	
				3.6838	.0058		
	H_2SO_4	"	"	3.7592	.0009	.0411	
				3.2601	.0019		
Duplicate on sample above	HNO_3	25°C	24 Hrs.	5.0766	.0006	.0118	These samples illustrate well the unreliability of testing samples to determine their relative resistance to deterioration by means of their solubility in acids.
				5.0832	.0000		
	HCl	"	"	4.3619	.0084	.191	
				3.6778	.0062		
	H_2SO_4	"	"	3.7583	.0005	.0312	
				3.2482	.0016		
Triplicate on sample above.	HNO_3	25°C	24 Hrs.	5.0760	.0005	.0077	
				5.0832	.0008		
	HCl	"	"	4.3525	.0186	.395	
				3.6715	.0134		
	H_2SO_4	"	"	3.7578	.0015	.061	
				3.2466	.0027		

Table 6.

Relative Solution of Alloys containing Ni.-Cr.-Al. and Fe. in Acids.

Description of Sample.	Acid.	Temp.	Time.	Wt. Taken	Wt. Dissolved	Per. Cent Dissolved	Remarks.
Wire . 16 m/m Ni. - 79 %. Cr. - 20 % Al. - 1.0 % Fe. - Trace.	HNO_3	25°C	24 Hrs	.0228	.0010	5.8 Z	All acid used in experiment 3 was composed of one part concentrated acid to three part 3 water.
				.0205	.0013		
	HCL	"	"	.0290	.0027	8.67	
				.0273	.0022		
	H_2SO_4	"	"	.0325	.0007	2.04	
				.0207	.0004		
Wire . 8 m/m Ni. - 79 %. Aprox. Cr. - 20 %. Al. - 1.0 %. Fe. - Trace	HNO_3	26°C	24 Hrs	.1790	.0222	13.07	This sample had the same composition as the one above, but was of different size, the area does not vary directly as the percent by weight dissolved-
				.1769	.0247		
	HCL	"	"	.1861	.0068	3.35	
				.1871	.0057		
	H_2SO_4	"	"	.1798	.0010	.586	
				.1798	.0011		
Wire. 8 m/m Ni. - 80 Cr. - 20 Aprox.	HNO_3	25°C	24 Hrs	.1777	.0021	1.008	The absence of Fe. and Al. seems to decrease the solubitiy of this alloy.
			"	.1792	.0015		
	HCL	"	"	.1749	.0019	.944	
				.1745	.0014		
	H_2SO_4	"	"	.1812	.0004	.197	
				.1721	.0003		

Table No 7

R. S. Howard '10

Relative Rates of Solution of Alloys. #1.

Sample.	Acid.	Temp.	Time	Wt. Taken.	Wt. Dissolved.	Per Cent Dissolved	Ave % Dissolved
Monel Metal. Ni. – 68-72 Fe. – 0.5-1.5 S. – 0.14 C. – .073 – .15 Cu. – Balance. Cast, – Sp. Gr. 8.86 Rolled – Sp. Gr. 8.94	HNO_3	25°C	Hrs 120	9.3786	.7990	8.15	~~19~~
				9.9917	3.0364	30.35	
	HCl	"	" "	8.8798	.0448	.504	.514
				8.3557	.0437	.523	
	H_2SO_4	"	" "	7.1403	.0126	.177	.181
				8.7514	.0162	.185	
	HNO_3	25°C	Hrs. 48	8.5796	.1499	1.75	0.965
				6.9553	.0125	.180	
	HCl	"	" "	8.8350	.0054	.061	.060
				8.3120	.0050	.060	
	H_2SO_4	"	" "	7.1277	.0024	.033	.028
				8.7352	.0021	.024	
	HNO_3	25°C	Hrs. 24	8.4297	.0296	.351	.619
				6.9428	.0611	.880	
	HCl	"	" "	8.8296	.0041	.046	.049
				8.3070	.0044	.053	
	H_2SO_4	"	" "	7.1253	.0014	.019	.021
				8.7331	.0020	.023	
	HNO_3	100°C	Min 10	8.4001	.0296	.352	.619
				6.8817	.0611	.887	
	HCl	"	" "	8.8255	.0039	.044	.048
				8.3026	.0044	.053	
	H_2SO_4	"	" "	7.1239	.0014	.019	.021
				8.7311	.0020	.023	

Remarks.

From the table it is shown that with monel metal after the first 24. hours at 25°C or 10 min. at 100 °C the solvent action of the acid is slow.

Table 8

E.J. Howard 10

CONTINUED. #2.

SAMPLE	ACID	TEMP	TIME	WT TAKEN.	WT. DISSOLVED.	PER.CENT DISSOLVED.	AVE % DISSOLVED.	REMARKS
FERRO SILICON.	HNO_3	25°C	HRS. 24	0.0951	.0002	0.21	0.105	FERRO SILICON SHOWS GREAT VARIATION IN ITS SOLUBILITY.
				0.1070	.0000	0.00		
	HCL	"	"	0.1060	.0000	0.00	0.00	
				0.1011	.0000	0.00		
	H_2SO_4	"	"	0.0742	.0001	0.135	0.107	
				0.1262	.0001	0.079		
	HNO_3	100°C	MIN. 10	0.0949	0.0000	0.00	0.00	
				0.1070	0.0000	0.00		
	HCL	"	"	0.1060	0.0002	0.185	0.190	
				0.1011	0.0002	0.195		
	H_2SO_4	"	"	0.0741	0.0000	0.000	0.039	
				0.1261	0.0001	0.079		
ALUMINIM COPPER AL. - 90% CU. - 100%	HNO_3	25°C	HRS 24	5.0827	.1684	3.30	3.54	HCL HAD VIGIOROUS ACTION NO COPPER COLOUR OF SOLUTION A SOFT SPONGY SUBSTANCE WAS LEFT ON OUTSIDE OF THE SAMPLE WHICH WAS COPPER, COLOORED. THIS WAS PROBABLY SILICIC ACID.
				4.4490	.1686	3.79		
	HCL	"	"	4.1250	4.1250	100.00	100.00	
				4.8295	4.8295	100.00		
	H_2SO_4	"	"	4.3706	.0616	1.41	1.38	
				4.1650	.0561	1.35		

TABLE NO 8

R. J. HOWARD

CONTINUED. #3.

SAMPLE.	ACID.	TEMP.	TIME.	WT. TAKEN.	WT. DISSOLVED.	PER CENT. DISSOLVED	AVE % DISSOLVED	REMARKS.
COMMERCIAL. ALUMINUM	HNO_3	25°C	HRS 24.	4.1394	.0234	.515	5145	THE ADDITION OF SILICON TO ALUMIUM IS DETREMENTAL SO FAR AS ITS PREVENTION OF THE METAL FROM SOLUTION IN ACIDS IS CONCERNED.
				4.7514	.0244	.514		
	HCL	" "	" "	3.8781	3.8781	100.00	100.00	
				4.2865	4.2865	100.00		
	H_2SO_4	" "	" "	3.2895	.0091	.276	.247	
				2.5109	.0051	.219		

TABLE No 8

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